



Early metakaolin reactions in pozzolanic R^3 -test: calorimetry baseline correction of initial temperature jump due to ex-situ mixing

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Abstract The increasing concerns regarding global warming and the scarcity of raw materials in the construction industry have led to a growing need for alternative low-carbon binders to partially replace ordinary Portland cement. To assess the suitability of pozzolans as supplementary cementitious materials (SCMs), the R^3 -test has been introduced and successfully validated for a wide range of materials. This test provides an opportunity to analyze the reactivity classification and study the reaction mechanisms and kinetics of novel SCMs in a well-controlled environment. In this study, the focus lies on evaluating the early reactions of lime paste samples through isothermal calorimetry tests conducted at 40 °C. However, conventional mixing methods present experimental challenges. In-situ mixing fails to achieve proper paste homogenization, while ex-situ mixing results in a temperature difference at the start of testing due to the elevated testing condition of 40 °C. To address these concerns, a novel calorimetric methodology is proposed for early detection of reactivity responses. The main concept involves establishing a baseline correction for the temperature difference caused by ex-situ

mixing, which is calibrated using an inert sample. This correction allows for the extraction of the heat generated by the early reactions. Combined with the Tian time correction, this methodology enables the evaluation of early reactions in lime paste samples measured with isothermal calorimetry at 40 °C within the first 100 min after mixing. The effectiveness of this methodology was demonstrated by evaluating the early reactions and the impact of potassium sulfate on three different types of metakaolin.

Keywords R^3 -test · Isothermal reaction calorimetry · Tian correction · Metakaolin · Supplementary cementitious materials · Early pozzolanic reactions

1 Introduction

The increasing global interest in alternative binder materials is due to global warming and raw material shortages in the construction industry. In order to assess the suitability of novel materials for the use as supplementary cementitious materials (SCMs) standardized testing procedures are needed [1, 2]. In this context, Avet et al. introduced the R^3 -test (rapid, relevant, reliable) in 2016 [3] that was further optimized and validated over a wide range of materials [4, 5]. With the R^3 -test it is possible to classify the raw

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materials by testing their reactivity in an alkaline suspension after seven days stored at 40 °C [5]. The reactivity can be measured through various testing procedures. Meanwhile, determining the bound water content using an oven test, as well as calculating the overall heat release from isothermal calorimetry, have been suggested [1, 4].

In addition to the defined composition of the R³-samples, a wider variety of sample compositions can be utilized to acquire more comprehensive insights into the mechanisms and kinetics of the pozzolanic reactions of specific SCMs. The main objective of this approach is to investigate the SCM reactions in a well-defined and controlled environment. Emphasis is on comprehending the fundamental phase (trans)formations and their kinetic behavior while minimizing the influence of additional factors that may be present in more complex cementitious systems. For this purpose, isothermal calorimetry seems to be a promising testing procedure. When conducting calorimetry at 40 °C with lime paste samples similar to the R³-test, two main experimental issues were identified, namely (a) in-situ mixing challenges to achieve a good homogenization as the alkaline suspension cannot be introduced by a syringe and (b) ex-situ mixing leads to a temperature difference due to the elevated testing temperature of 40 °C. Even when the materials are preconditioned at 40 °C prior to mixing, practically it is challenging to provide reproducible conditions for each sample as the sample temperature inevitable drops during the mixing process. Mixing in a water bath seems like another opportunity, but is elaborated and intermediate steps are also difficult to control. To omit the initial heat release peaks that are affected by thermal equilibration of the sample the R³-test procedure (used to classify different SCMs according to their total reactivity) recommends to calculate the cumulative heat release starting from 1.2 h (72 min) after mixing [4]. Mixing the samples at 40 °C using a water bath, did not change the test results from 72 min onwards [4], indicating that the temperature difference effect does not affect the data gained after 72 min.

For a deeper understanding of the reaction mechanisms and kinetics of novel SCMs, especially for fast reacting materials, the very early reactions occurring within the first 72 min of the experiment could be of interest. To address the temperature difference effect during the early testing times, this article provides an

experimental testing procedure for lime paste samples similar to R³-samples with isothermal calorimetry and introduces a novel methodology approach. It proposes to mix the samples ex-situ, in order to achieve good homogenization, but at ambient temperature, where an inert sample of the alkaline suspension (without added SCM) is used for a baseline correction. The methodology is based on separating the temperature difference effect, obtained from an inert sample and subtract it from the reactive one to obtain the heat generation response related to the early reaction processes. In isothermal calorimetry, the accurate recording of fast reaction processes can be influenced by a time-lag resulting from the thermal inertia between the sample and the calorimeter instrument. To address this issue, the Tian correction method has been introduced in the existing literature [6, 7]. Whenever employing the Tian correction method for the time-lag between initial and actual recording of the isothermal calorimetry, the rapidly liberated reaction heat of these lime paste samples can be monitored during the initial 100 min after mixing. This approach turned out to be very successful when studying fast reactions in calorimetry at a temperature of 40 °C. The method was demonstrated by evaluating the reproducibility of a baseline and early reaction mechanisms using three different types of metakaolin, as well as exploring the impact of potassium sulfate on the metakaolin reaction. Initial reactions of metakaolin with calcium hydroxide as well as with sulfates and/or carbonates are of particular interest, as various hydrate phases may form and transform that influence the binders performance, e.g. in terms of rheology [8, 9]. In lime-based pastes with metakaolin, sulfate incorporation rapidly forms ettringite [3, 10–18], which may convert to monosulfoaluminate (C₄AsH₁₂; AFm) [3, 12, 14, 19, 20] depending on sulfates and reaction time, while additional carbonates stabilize ettringite by the formation of hemi- and monocarboaluminates (C₄Ac_{0.5}H₁₂ and C₄AcH₁₁; CO₃-AFm) [3, 11, 15, 21–23].

2 Experimental program

R³-samples consist of an alkaline suspension homogeneously mixed with a powdered SCM. As the focus of this study is on the early reactions (first 100 min), metakaolin was chosen as SCM in this study due to its



Table 1 Composition of 100 g alkaline suspension with (R3) [3] and without (0.32KOH) potassium sulfate

Suspension	Ca(OH) ₂	K ₂ SO ₄	KOH	H ₂ O
R3	37.77 g	1.48 g	0.32 g	60.43 g
0.32KOH	38.34 g	–	0.32 g	61.34 g

high pozzolanic reactivity and the ability to form early ettringite in the presence of sulfates [3, 10–18, 20]. To demonstrate different intensities of early reactions, three different metakaolin were used and the alkaline suspension was prepared with (mix design according to [1, 3]) and without potassium sulfate.

The composition of 100 g suspension (R3) is outlined in Table 1 [1, 3] and consist of powdered calcium hydroxide ($\geq 96\%$), potassium hydroxide pellets ($\geq 85\%$), powdered potassium sulphate ($\geq 99\%$), and deionized water. For the preparation of 100 g suspension, potassium hydroxide pellets (KOH) were dissolved in 7 g deionized water for 15 min using a magnetic stirrer [24, 25]. In the next step, dissolved potassium hydroxide was homogenized with the remaining components (calcium hydroxide, potassium sulfate, and the remaining deionized water) using an electric mixer for another 15 min [24, 25]. To evaluate the effect of sulfates in the first minutes of reaction, an additional alkaline suspension was prepared without potassium sulfate according to Table 1 (0.32KOH).

To study the temperature jump effect on inert samples, eight calorimetry samples of alkaline suspension (without SCM) were prepared with (R3) and without (0.32KOH) potassium sulfate (4 for each suspension). The weighing for the reactive samples was chosen to 20.0 g \pm 0.3 g. Equivalent heat capacities of inert samples were obtained by adjusting the weight of each type of inert suspension (R3 and 0.32KOH) to match the heat capacity of the reactive samples, namely 18.56 g \pm 0.1 g for R3 and 18.39 g \pm 0.1 g for 0.32KOH (_1). To analyze the effect of deviations from that target value, the following weights for three more samples for each inert suspension were chosen as 16.0 g \pm 0.3 g (_3), 18.0 g \pm 0.3 g (_2) and 20.0 g \pm 0.3 g (_4), respectively. To study the potential impact of different inert samples on the baseline correction curve, an additional

test series, named “inerts”, was conducted. This series also includes water samples as a control for the R³-suspensions (without SCM). Three specimens were measured for each type of inert sample, and the weighing process was adjusted accordingly to achieve the same heat capacity for each sample.

Three types of industrially produced metakaolin were used in this study. They differ mainly in their amount of amorphous content (MK1 \sim 68 wt% < MK2 \sim 83 wt% < MK3 \sim 98 wt%) as well as the amount and type of incorporated impurities. Their chemical compositions are summarized in Table 2. Thermogravimetric analysis (TGA) of the raw materials shows a mass loss of around 2.2 wt% for MK1 in the DTG-curve between \sim 450 and 700 °C (Fig. S1 in the Supplementary Material) indicating a lower calcination temperature (< 450 °C) that leads to a lower dehydroxylation degree compared to MK2 and MK3. Powder X-ray diffraction (XRD) results confirm the presence of remaining kaolinite in MK1 together with impurities like quartz, cristobalite and goethite (Fig. 1). Other minerals present as impurities in MK2 comprise of muscovite, quartz and anatase, whereas MK3 is an almost pure metakaolin with only small traces of muscovite and anatase (Fig. 1). TGA of the raw materials was carried out with “STA 449 F5 Jupiter” from NETZSCH (Selb, Germany) with nitrogen as an inert gas. 40–50 mg of powdered sample was placed in alumina crucibles, heated up to 40 °C, kept constant for 30 min and then heated up to 1000 °C at a constant heating rate of 20 °C per minute. XRD of the three metakaolin was carried out with “Bruker D2 Phaser” from Bruker Corporation (Billerica, USA), configured with CuK α 1,2 radiation (40kV and 10mA), linear Lynxeye detector (5 degrees opening). All raw material samples were measured with 0.02 two theta step size and measurement time of 2 s per step.

Both the alkaline suspension and the reactive samples, which are a mixture of the suspension and metakaolin, were prepared in a temperature-controlled laboratory at approx. 20 °C, and the metakaolin used in the mixing process was also stabilized (overnight) at the same temperature. For the samples with potassium sulfate (_R3), 50 g suspension (R3, Table 1) was mixed with 6.30 g metakaolin (MK1, MK2 and MK3) according to [3] for 3 min with an electric stirrer [25]. The samples without potassium sulfate (_0.32KOH) were prepared with 6.39 g per 50 g suspension



Table 2 Amorphous contents and chemical compositions of the used metakaolin in wt%

	Amorphous	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂
MK 1*	~ 68	53–54	41–44	< 0.5	n/a	n/a	n/a	< 1.0	n/a
MK 2	~ 83	53.0	42.2	2.4	< 0.5	< 0.5	< 0.5	< 0.5	1.8
MK 3*	~ 98	52.3	45.2	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	1.7

*Chemical compositions according to the manufacturer

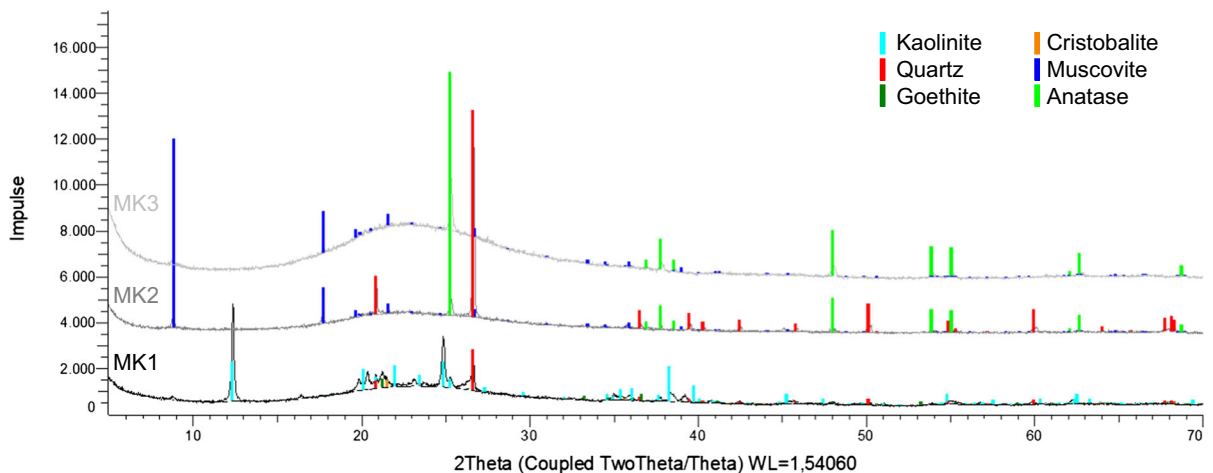


Fig. 1 Powder X-ray diffractogram and qualitative analysis of the three different metakaolin samples used in this study (bottom: MK1, middle: MK2 and top: MK3)

(0.32KOH, Table 1) to keep the metakaolin (MK) to calcium hydroxide (CH) weight ratio at 0.33 as well as the water to binder ratio (binder = MK + CH) constant at 1.2. Furthermore, to evaluate the repeatability of the proposed methodology, a test series named “MK3_Rep” was introduced, consisting of three similar specimens. The metakaolin type MK3 in combination with the suspension R3 (as defined in Table 1) was used for this series. For each reactive sample in this study, 20 g ± 0.3 g was weighed in the calorimetry plastic ampoule and placed immediately in the measurement channel chamber. The temperature at sample placement in the calorimeter was not measured to minimize the time-lag between mixing and sample placement, aiming to reduce temperature differences between the inert and reactive samples. After sufficient stabilization time (overnight) of the components, each sample was weighed for 3 min ± 30 s, recording the mass with a tolerance of 0.001 g. The initial sample temperature (during sample loading) could slightly vary due to the mixing procedure and initial dissolution reactions within the first 3 min.

The proposed short and consistent mixing procedure minimized the first effect and was considered in the baseline correction. The second effect provided an approximate indication of the heat of reaction. Therefore, small deviations in sample temperatures from the room temperature had negligible effects on the baseline correction. This was confirmed by calculating the temperature difference between the initial temperature and the testing temperature of 40 °C for the inert samples, as shown in Table 3 and discussed in detail in Sect. 3.1. The temperatures were calculated using Eq. (1) and heat flow measurements, as direct experimental measurement of these temperatures posed challenges.

“MC CAL” from C3 Prozess- und Analysetechnik GmbH (Haar, Germany) was used for the calorimetry measurements. The device was preconditioned and calibrated at 40 °C, water was used as a (differential) reference sample and data was collected every 30 s for 7 days. For some parts of this study, data was collected every 1 s, namely for the tests to determine the Tian constant (Sect. 3.2) as well as for

an additional test series (sample named by adding the suffix “_ats”, data shown in Sect. 4), where MK3 with and without potassium sulfate was tested a second time.

3 Methodology

The calculation approach assumes, that the initial temperature jump effect could be obtained as a baseline measurement of an inert sample and subtracted from the reactive one. The effect is due to the lower sample temperature of $\sim 20\text{ }^{\circ}\text{C}$ compared to the testing temperature of $40\text{ }^{\circ}\text{C}$, that enables a convenient ex-situ sample preparation at ambient temperatures with all samples having the same initial temperature. As discussed in Sect. 3.1, to ensure accuracy and consistency, an additional inert sample (here: alkaline suspension without SCM) with a similar heat capacity as the reactive samples must be employed for the baseline correction that accounts for the initial temperature jump. This can be achieved by adjusting the sample weighing accordingly. The type of inert material was found to have no significant effect on the proposed methodology, as demonstrated in Fig. 3 (comparison between water and suspension) and discussed in Sect. 3.1.

3.1 Baseline correction due to initial temperature jump

Due to the temperature difference of $\sim 20\text{ }^{\circ}\text{C}$, when the sample was mounted, there is a significant drop in the measured heat flow to highly negative values. This is followed by an exponential increase in the signal until it approaches zero (for the inert sample) that takes approx. 100 min.

To verify this approach, the temperature difference of $\sim 20\text{ }^{\circ}\text{C}$ can mathematically be calculated from the heat generated in the experiment by using the fundamental caloric equation (Eq. 1). Table 3 summarizes the temperature differences of the eight inert samples calculated from the measurement data as integral over the first 100 min, resulting in a mean value of $-20.1\text{ }^{\circ}\text{C}$ and a standard deviation of $0.7\text{ }^{\circ}\text{C}$.

$$Q = cp \cdot m \cdot \Delta T \quad (1)$$

Q : (Measured integral) heat in J, cp : Specific heat capacity in $\text{J}/(\text{g K})$, m : Mass in g, ΔT : Temperature difference in K.

Testing of inert samples with different heat capacities in this study shows that the temperature adjustment in terms of time and intensity is dependent on the samples heat capacity. The heat capacity was calculated by multiplying the individual mass of the sample with the specific heat capacity, determined according to the sample composition while assuming specific heat capacities for solids ($0.80\text{ J}/(\text{g K})$) and water ($4.18\text{ J}/(\text{g K})$). The temperature equilibration speed, called time constant in this study should not change significantly within the acceptable deviations of the masses. A higher deviation in masses is desirable to lower the weighting time to minimize changes in sample (room) temperature. To calibrate the initial baseline and the time constant (analogously to the Tian constant determination in Sect. 3.2) several inert samples, that have a range of heat capacity comparable ($+4.5\text{ J/K}$ and -7.1 J/K) to the reactive samples ($52.4\text{--}53.5\text{ J/K}$) have been tested. Results show small deviations for the range marked with a red circle in Fig. 2 ($+4.5\text{ J/K}$ and -1.3 J/K). As the exact weighing is practically not possible in a short time period, the mass (i.e. heat capacity) is a critical factor for the good calibration. According to Fig. 2, the inert sample should have a similar heat capacity compared to the reactive samples and the weight needs to be calculated prior to analysis. Thus, small variations in heat capacity due to weighing accuracy can be corrected mathematically using a multiplication factor (see *C-factor* below). The validity of this approach is strengthened by the results obtained from the “inerts” test series. In this series, six inert samples comprising of three water samples and three samples of alkaline suspension with comparable heat capacities were examined in detail. The mean values of these baselines, each normalized to the respective sample heat capacity, are shown in Fig. 3 together with the standard deviations. Figure 3 illustrates only minor deviations within the first 5–10 min of the experiment, confirming that the choice of inert material has no significant impact on the (normalized) baseline. Thus, the consistent results obtained from the “inerts” test series further substantiate the robustness of the proposed approach. The results also demonstrate that higher deviation of heat capacity from the reactive



Table 3 Calculated temperature difference at time of sample mounting in °C calculated from Eq. (1) and measured integral heat over the first 100 min resulting in a mean value of -20.1 °C ($s = 0.7$ °C)

Suspension	0.32KOH	R3
Calculated temperature difference	-19.5 (_1)	-20.0 (_1)
	-20.8 (_2)	-19.7 (_2)
	-21.6 (_3)	-19.8 (_3)
	-19.9 (_4)	-19.1 (_4)

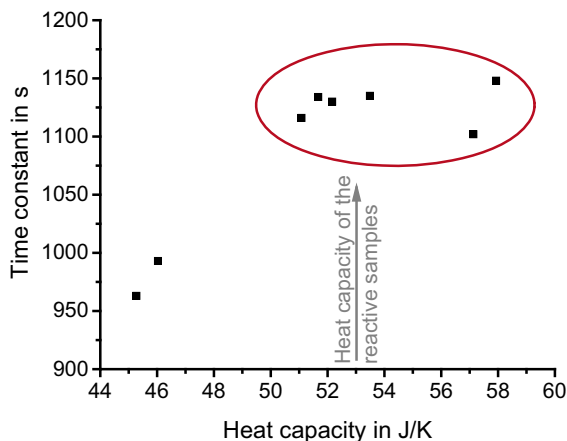


Fig. 2 Time constants determined (according to the Tian method) for different inert samples calculated from the start of the measurement with $\Delta T \sim 20$ °C. Inert samples in the (relatively small) heat capacity range of the reactive samples (marked with a red circle) show a similar time dependent behavior

sample has a significant impact on the calibration of the time constant; resulting in the two outliers observed for the “too low” heat capacity (Fig. 2). Furthermore, to ensure accurate results, it is recommended to measure both the inert and the reactive samples within the same test series. This will guarantee identical temperatures for both material storage and sample preparation as this methodology is sensitive to small temperature variations. It even holds for temperature-controlled rooms, where slight variations in temperature may occur, even as the water temperature used to clean the mixing equipment, which should be taken into consideration as well.

The proposed interpretation utilizes raw calorimetry data beginning with the lowest (most negative) value, incorporating effects from both the temperature adaption (of inert and reactive samples) and heat generated by the reactive samples. To extract the heat

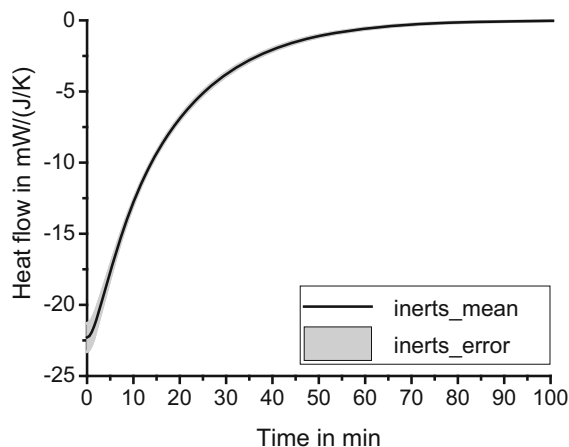


Fig. 3 Temperature difference effect as mean value (inerts_mean) and standard deviation (inerts_error) of six inert samples from the “inerts” test series including 3 water samples and 3 with alkaline suspension with heat capacities in the range of the reactive samples (normalized to the individual heat capacity)

generated specifically by the reaction processes, one must eliminate the baseline effects of the temperature jump. This is achieved by calibrating the inert sample and using it as a baseline for comparison with the reactive samples. The baseline signal is then subtracted from the reactive samples signal to obtain the heat generated specifically by the reaction processes. For this calculation, the (slightly) different heat capacities of the reactive and the inert samples need to be addressed, arising from the specified mass measurement tolerance (and weighing time limits). For this purpose, the *C-factor* was defined according to Eq. (2). The specific heat capacities (*cp*) of the inert (exemplarily shown on suspension “R3” according to Table 1) and the reactive (12.59 g SCM in 100 g suspension according to [3]) samples can be calculated according to Eqs. (3) and (4) by taking into account the respective sample compositions as well as the



assumed specific heat capacities for solids (0.80 J/(g·K)) and water (4.18 J/(g·K)). Equation (4) is based on the R³-sample composition consisting of 100 g suspension (R3) along with 12.59 g metakaolin.

$$C\text{-factor} = \frac{C_{\text{reactive}}}{C_{\text{inert}}} = \frac{cp_{\text{reactive}}}{cp_{\text{inert}}} \cdot \frac{m_{\text{reactive}}}{m_{\text{inert}}} \quad (2)$$

C-factor: Defined calculation factor to address the (slightly) different heat capacities of the reactive and inert sample due to (time) limited mass measurement accuracy, *C*: Heat capacity in J/K, *cp*: Specific heat capacity in J/(g K), *m*: Weight of the sample in g, *inert*: Referring to the inert sample, *reactive*: Referring to the reactive sample.

$$cp_{\text{inert}} = 0.3957 \cdot 0.80 \text{ J/(g} \cdot \text{K)} + 0.6043 \cdot 4.18 \text{ J/(g} \cdot \text{K)} = 2.8425 \text{ J/(g} \cdot \text{K)} \quad (3)$$

$$cp_{\text{reactive}} = cp_{\text{inert}} \cdot \frac{100}{112.59} + 0.80 \text{ J/(g} \cdot \text{K)} \cdot \frac{12.59}{112.59} = 2.6141 \text{ J/(g} \cdot \text{K)} \quad (4)$$

With the help of the *C-factor* and following the assumptions explained above, the heat flow of the reactive sample induced by dissolution and reaction processes can be calculated according to Eq. (5).

$$\dot{Q}_{\text{inert-corrected}} = \dot{Q}_{\text{raw}} - C\text{-factor} \cdot \dot{Q}_{\text{inert,raw}} \quad (5)$$

$\dot{Q}_{\text{inert-corrected}}$: Data of heat flow in mW (baseline corrected due to initial temperature jump), \dot{Q}_{raw} : Raw data of heat flow in mW (started from lowest value), $\dot{Q}_{\text{inert,raw}}$: Raw data of heat flow of the inert sample in mW (started from lowest value).

3.2 Tian correction

To account for the time-lag caused by thermal inertia effects between the samples and the calorimeter instrument, the Tian correction method [6, 7] is particularly necessary, especially for rapidly changing reaction rates observed during the initial stage of the experiment. The Tian constant plays a crucial role in this correction method, as it characterizes the exponential decay of a signal. Specifically, it represents the time required for the signal to decrease from any given value to 36.8% ($\exp(-1)$) of that value [7]. Incorporating the Tian correction ensures accurate alignment of the signals and compensates for the thermal inertia

effects, allowing for more accurate interpretation of the experimental data.

One option to determine the Tian (time) constant is to thermally disturb a sample when the heat flow is constant or low, e.g. by quickly lifting and again placing the ampoule in the calorimeter [7]. The 12 calorimetry ampoules, with heat capacities ranging from 45.3 to 57.9 J/K, were promptly removed from the chamber and then reinserted at the end of the measurement after 7 days. Moreover, different “lifting” times (time between lifting the sample and again placing it in the chamber) were investigated, namely 1, 6, 13 and 30 s, to address two opposing effects. First, the “lifting” time should be short to minimize a temperature difference due to sample cooling outside the chamber. Second, if the “lifting” time is too short, other effects, like e.g. cooling the stoppers and convection, become too dominant. The Tian constants are calculated individually for each calibration measurement, analyzing the exponentially decaying signal. As the Tian constant represents the time that the signal needs to decrease from any value to 36.8% ($\exp(-1)$) of that value [7], the curves were normalized to the lowest (initial) value and assuming an exponential relationship ($\dot{Q}_{\text{normalized}}(t) = -\exp(-t/\tau)$), the Tian constant τ was determined for a heat flow of $-\exp(-1)$ where time $t = \tau$ [7] (Fig. 4). The results as mean values over 12 samples with measurement uncertainty (\pm one standard deviation) are visualized in Fig. 5. The standard deviation decreased

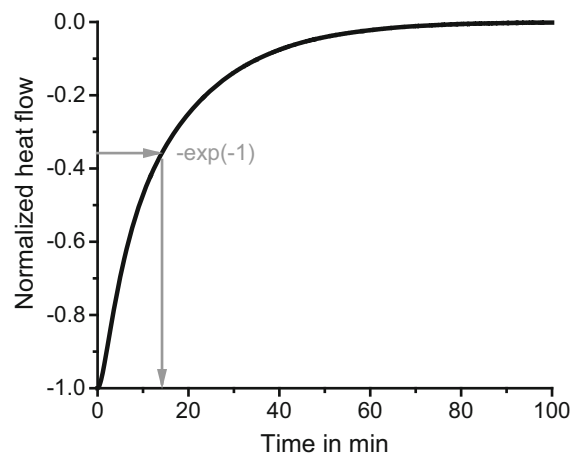


Fig. 4 Tian constant determination (Data of R3_1 shown exemplarily for 30 s “lifting” measurement; heat flow normalized between the null-baseline and -1 as the lowest measured value)

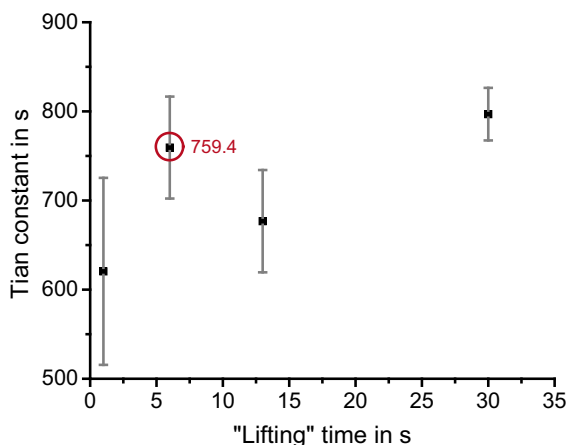


Fig. 5 Tian constants as mean values over 12 replicate measurements for different “lifting” times (Tian constant used for the correction in this study marked in red)

remarkably from a “lifting” time of 1–6 s. To reduce the influence of (initial) convection for the Tian constant determination, the mean value of 759.4 s from this experiment (6 s) was further used for the Tian correction in this study.

The heat flow values of each sample \dot{Q} were Tian-corrected with the Tian constant τ (= 759.4 s) according to Eq. (6).

$$\dot{Q}_{\text{Tian-corrected}} = \dot{Q}_{\text{inert-corrected}} + \tau \cdot \frac{d\dot{Q}_{\text{inert-corrected}}}{dt} \quad (6)$$

$\dot{Q}_{\text{Tian-corrected}}$: Tian corrected heat flow in mW,
 $\dot{Q}_{\text{inert-corrected}}$: Data of heat flow in mW (baseline corrected due to initial temperature jump), τ : Tian constant.

4 Results and discussion

Figure 6 shows the heat flow of all tested sample compositions up to 100 min calculated according to the proposed new methodology approach described in Sect. 3. Heat flow results are normalized per gram of metakaolin. Up to three peaks are visible in the first 100 min depending on the sample composition. The first exothermic peak (1) occurs within the first approx. 25 min and seems to be due to the dissolution of metakaolin. The second peak (2) occurs as a smaller hill in between the two other peaks for MK2 and is

visible in the data for MK3 with and without potassium sulfate as a shoulder on the third peak. MK1 does not show this characteristic. The third peak (3) occurs from approx. 25 min (depending on the sample composition) to 100 min. When comparing the three different metakaolin types, MK1 shows no distinct peaks in this initial time frame, but the first dissolution (peak 1). When no potassium sulfate is present in the sample (MK3 + 0.32KOH suspension = MK3_noK₂SO₄), peak 2 appears approx. 10 - min earlier. MK2 and MK3 have similar intensities of peak 3, but for MK2 the peaks (2 and 3) start slightly earlier and overlap more. For the MK3 sample without potassium sulfate (MK3_noK₂SO₄), peak 3 is lesser pronounced and earlier compared to MK3 with sulfates. As the characteristic pattern of these three peaks is observed to be independent of the sulfate presence, they cannot be due to ettringite formation only, but indicate to other reaction processes, like e.g. hemi- and/or monocarboaluminate formation due to carbon dioxide contamination from air exposure [11, 13, 14, 17, 21, 26–28].

To further demonstrate the capability of using the proposed novel methodology, the reproducibility of the sample preparation was qualitatively investigated on two test series incorporating MK3 samples with and without potassium sulfate (additional test series named as _ats). The sample preparation process (suspension and reactive sample) in the additional test series (_ats) was even more precisely controlled with the aim to minimize carbonation contamination due to air exposure. Figure 7 compares the results of both test series. The first peak within the first 25 min (1) occurred in both test series with a comparable peak intensity but a slightly broader shape in the second test series (_ats). The broader first peak leads to the appearance of the second peak (2) as a shoulder on the first one. The third peak (3) is clearly present in the first test series, while not visible in the data originating from the additional test series (_ats). Thus, the third peak could be attributed to carbonate formations (hemi- and/or monocarboaluminates), arising from carbon dioxide exposure during sample preparation.

The heat flow of all tested sample compositions is shown in Fig. 8 for up to 36 h with characteristic peak formations. In general, the intensity of the heat flow increases with the amount of amorphous metakaolin content according to the following order: MK3 > MK2 > MK1 (in agreement with amorphous content



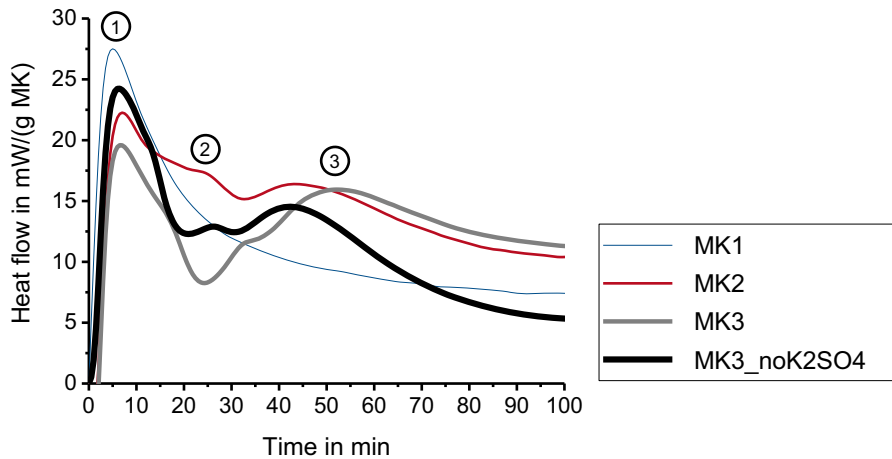


Fig. 6 Initial heat flow in mW/(g MK) of all tested sample compositions (MK1-MK3 and MK3 without potassium sulfate) up to 100 min

Fig. 7 Comparison of the heat flow of MK3 samples with and without (_noK2SO4) potassium sulfate originated from different test series (additional test series named as _ats) up to 100 min

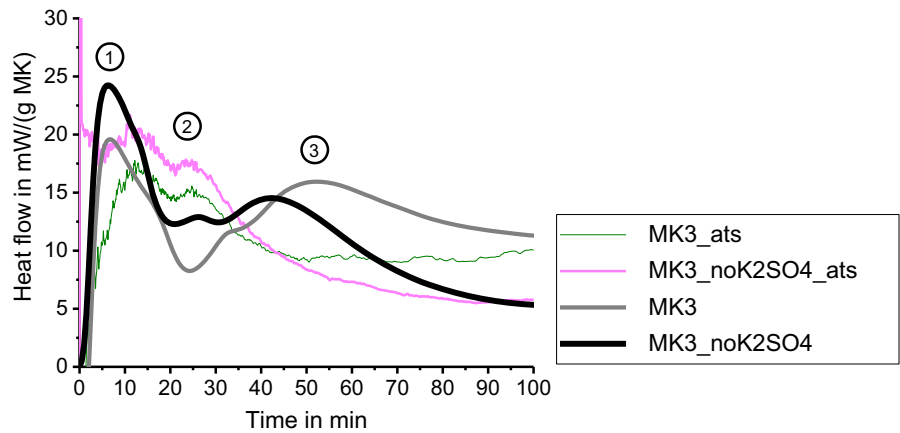
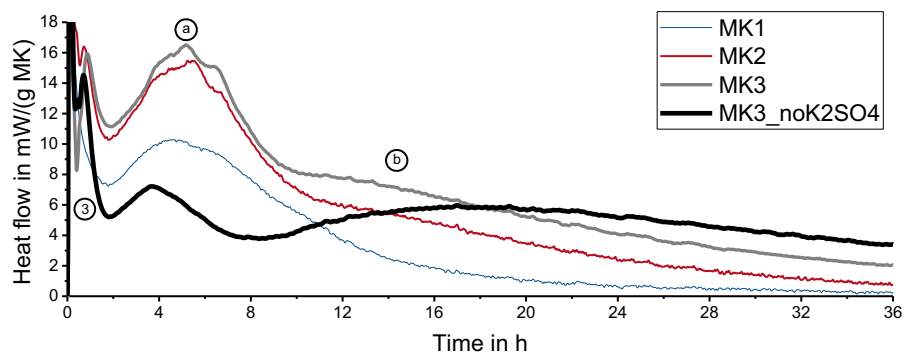


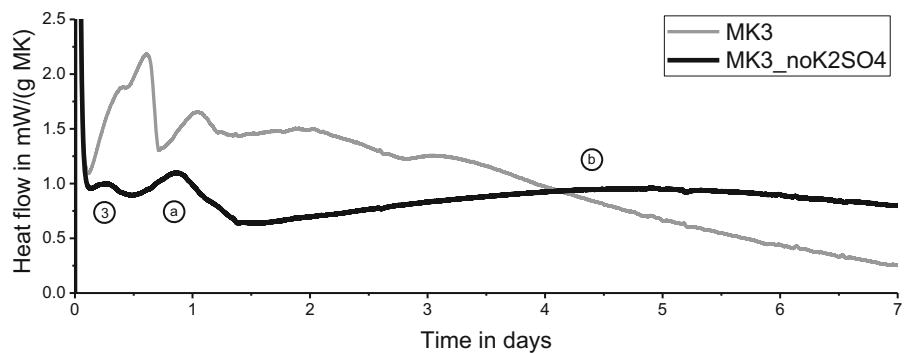
Fig. 8 Heat flow of all tested sample compositions up to 36 h at 40 °C



by XRD results, Table 2). From 100 min up to 36 h, all samples, except from MK1, show two main peaks. The first peak is composed of multiple different sub-peaks for samples with sulfates, while the maxima of both

main peaks are higher with potassium sulfate. The increased heat flow with potassium sulfate, especially within the first 12 h (a), demonstrates their importance on the early reactions of metakaolin. It can be

Fig. 9 Heat flow of MK3 with and without (noK_2SO_4) potassium sulfate up to 7 days at 20 °C



explained by higher rates of dissolution [12, 15] together with ettringite formation [3, 10–18, 20]. Without potassium sulfate, the last peak (b) is broader and shifted to later ages.

To qualitatively prove the presence of the peaks identified within the first 100 min with the proposed methodology (calorimetry at 40 °C), additional calorimetry measurements were carried out at 20 °C with MK3 with and without potassium sulfate. As there is no significant temperature difference of the initial sample temperature compared to the testing temperature and the reactions proceed much slower at 20 °C, the proposed methodology for data treatment was not that critical. The results are shown in Fig. 9. Qualitatively, the heat flow curves at 20 °C (Fig. 9) and 40 °C (Fig. 8) show similar shapes with the peaks occurring more separated and at later ages at 20 °C. The first peak observed at 40 °C from approx. 25 min to 100 min (3) was also observed (within the first 12 h) in the measurement at 20 °C, validating the presence of that heat flow peak that becomes detectable with the help of the proposed methodology.

As reaction kinetics are strongly temperature dependent and the temperature adaption from 20 to 40 °C takes approx. 100 min, the sample preparation in this study will result in different recorded signals compared to a sample preparation at elevated temperatures. Each sample first adapts to the testing temperature, so that the first reactions are slightly slower compared to a continuous measurement at 40 °C. The sample mounting with a large temperature difference is not in line with the general recommendations regarding calorimetry measurements [29]. However, as the elevated testing temperature of 40 °C is a specific characteristic of the R^3 -test, where a proper mixing can only be achieved ex-situ, the proposed methodology offers a user-friendly approach for

addressing the practical challenges. The temperature adaption from 20 °C to 40 °C in the calorimetry leads to highly negative heat flow values in the beginning, followed by an exponential decaying signal that slightly overshoots the zero baseline before it stabilizes. This observation can be explained by the disturbed heat sink temperature that needs some time to restore [7]. As it is a physical phenomenon, it occurs in the inert as well as the reactive samples, so it can be eliminated with the described correction calibration (subtraction of the inert from the reactive sample).

The proposed methodology offers a user friendly approach to effectively observe the early reactions of SCMs, here specifically tested on metakaolin in a controlled testing environment. More specifically, the materials considered in this testing environment are metakaolin (MK), portlandite (CH), alkali hydroxides and sulfates. The overall heat release data is shown in Fig. 10 and summarized for different reaction times in Table 4. Employing the proposed methodology led after 100 min to a cumulative heat release that ranges between 69.1 and 86.8 J/(g MK), depending on the composition of the sample and the type of metakaolin. Table 4 reveals that during the initial 100 min of testing, MK1 (MK3) exhibits 15.7% (7.8%) of the total heat released over a 7-days testing period. In Table 4, a comparison between the results obtained with and without (see *) the proposed methodology while excluding data from the first 72 min showed no significant difference in heat release. Contrarily to the regular R^3 -testing procedure [4], it should be noted that all results from this study are without preconditioning the raw materials at 40 °C before sample mixing. Moreover, the proposed methodology is of particular relevance whenever investigating the early reactions that occur within the first 72 min. Its importance lies in understanding the initial stages of



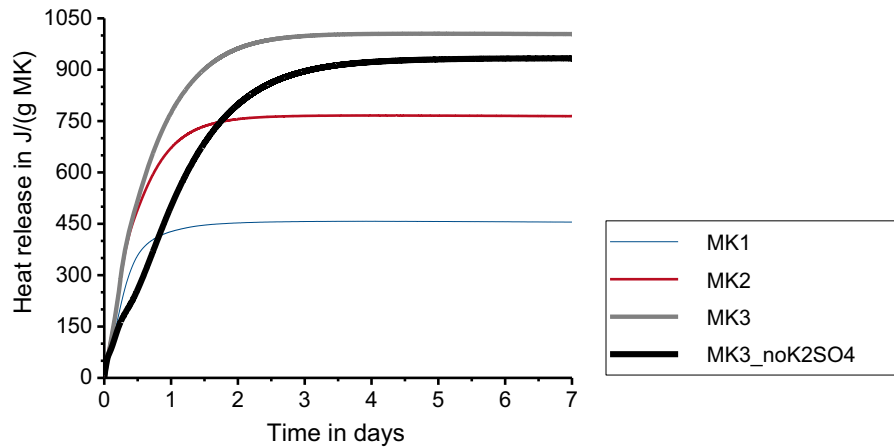


Fig. 10 Cumulative heat release in $J/(g \text{ MK})$ of all tested sample compositions (MK1-MK3 and MK3 without potassium sulfate) up to 7 days

Table 4 Summary of cumulative heat release (Q) after different reaction times and relative standard deviation (in%) calculated from the MK3_Rep test series

	MK1	MK2	MK3	MK3_noK ₂ SO ₄	Relative standard deviation (%)
Q(10 min) in $J/(g \text{ MK})$	13.7	8.9	7.6	10.9	51.1
Q(72 min) in $J/(g \text{ MK})$	56.9	68.1	57.5	58.7	12.7
Q(100 min) in $J/(g \text{ MK})$	69.7	86.8	77.8	69.1	10.0
Q(7 d) in $J/(g \text{ MK})$	445.5	764.8	1003.8	933.0	2.7
Q(100 min)/Q(7 d) · 100% in %	15.7	11.4	7.8	7.4	
Q(7 d) – Q(72 min) in $J/(g \text{ MK})$	398.6	696.7	946.3	874.3	
Q(7 d) – Q(72 min)* in $J/(g \text{ MK})$	399.6	701.8	952.1	877.1	

*Data not corrected according to this study

SCM reactivity rather than being essential for the overall SCM reactivity, as discussed in Sect. 1. Moreover, the proposed methodology enables a precise data analysis, including reaction kinetics and separation of peaks.

The repeatability of this experimental approach was assessed by three additional samples of MK3 in the R3 suspension (MK3_Rep test series). The mean heat flow values along with the corresponding standard deviations are shown in Fig. 11 up to 100 min reaction time. The results indicate significant deviations within the first 10 min, but show more consistent values with elapse of reaction process. The relative standard deviations of the total heat release at different reaction times are presented in the last column of Table 4. The data highlights that the heat recorded within the first 10 min provides a rough estimate, showing a variability

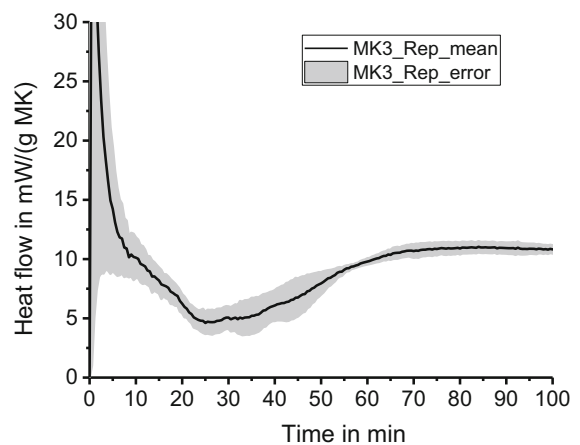


Fig. 11 Mean value of heat flow (MK3_Rep_mean) and standard deviation (MK3_Rep_error) of three replicates of MK3 tested in R3 suspension (test series “MK3_Rep”)

of 51.1%. However, as time progresses, the repeatability of the heat release measurements improves significantly. After 100 min, the variability decreases to only 10.0%, and after 7 days, it further decreases to 2.7%. This highlights the reliability and consistency of the measurements with increasing reaction time.

5 Conclusion

A new methodology has been developed for testing lime paste samples similar to R^3 -samples in calorimetry, which allows for identifying early reaction-induced heat flow in samples that is typically undisclosed. To achieve good homogenization, the samples were ex-situ mixed at ambient temperature. To correct for the initial temperature jump (testing temperature at 40 °C), an inert sample (here: alkaline suspension without SCM, but other inert materials are also possible) was used to establish a baseline. By applying the Tian correction to account for fast reaction processes, the proposed methodology allows for the quantification of the reaction heat (kinetics) in lime paste samples measured in calorimetry at 40 °C, even within the first 100 min, using a feasible ex-situ mixing process. This approach enables quantitative evaluation of early reaction kinetics of R^3 and similar lime paste samples, as demonstrated by studying the effects of three different metakaolin types (MK1, 2 and 3) and potassium sulfate addition. All three metakaolin types displayed a significant initial reaction peak within the first 25 min. Furthermore, the heat flow curves of MK2 and MK3 exhibit two additional peaks in the first 100 min after mixing. These characteristic peaks were also present for MK3 without potassium sulfate, although they appeared less intense (particularly peak 3) and earlier (peaks 2 and 3). The proposed methodology can be employed in future research and is recommended to explore the initial early reactions of metakaolin and/or other SCMs in controlled testing environments. This investigation is crucial for comprehending the fundamental phase (trans)formations that play a decisive role in determining various properties, such as the workability and placement (fresh rheological) characteristics of lime and/or alternative cement-based binders.

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Declarations

Conflict of interest The authors declare no conflicts of interest.

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